accomplished by trapping these compounds on adsorbents, followed by extraction with organic solvents.

Future Developments

GC will continue to be the main chromatographic technique used in herbicide residue analysis in the near future, due to the high sensitivity and selectivity given by the detectors that can be coupled with this technique. In particular, the use of less expensive and more robust and sensitive GC-MS equipment will keep growing in the routine determination and confirmation of herbicide residues.

The time needed for sample processing is expected to be reduced as a consequence of the continuation in the development of automatic processes for sample preparation, extraction and clean-up. These processes will use less sample and lower volumes of organic solvents in the analytical procedure.

New improvements in the gas chromatographic equipment to allow higher injection volumes of less purified extracts can also be expected.

See Colour Plate 85.

See also: **II/Chromatography: Gas:** Detectors: Mass Spectrometry; Detectors: Selective. **Insecticides:** Gas Chromatography. **Pesticides:** Supercritical Fluid Chromatography; Gas Chromatography. **Solid-Phase Matrix Dispersion: Extraction. III/Sorbent Selection for Solid-Phase Extraction.**

Further Reading

Barceló D and Henion MC (1997) *Trace Determination of Pesticides and their Degradation Products in Water*. Amsterdam: Elsevier.

Blau K and King GS (eds) (1978) *Handbook of Derivatives for Chromatography*. London: Heyden.

Dobrat W and Martijn A (eds) (1998) *CIPAC Handbook*: *Vol. H Analysis of Technical and Formulated Pesticides*. Cambridge: Black Bear Press.

Hutson DH and Roberts TR (eds) (1987) *Progress in Pesticide Biochemistry and Toxicology*, vol. 6 *Herbicides*. New York: Wiley.

Milne GWA (1995) *CRC Handbook of Pesticides*. Boca Raton: CRC Press.

Nollet LML (ed.) (1996) *Handbook of Food Analysis*. New York: Marcel Dekker.

Sherma J (ed.) (1989) *Analytical Methods for Pesticides and Plant Growth Regulators*: vol. XVII. *Advanced Analytical Techniques*. San Diego: Academic Press.

Tadeo JL, Sánchez-Brunete C, García-Valcarcel AI *et al.* (1996) Review: determination of cereal herbicide residues in environmental samples by gas chromatography. *Journal of Chromatography A* 754: 347.

Tekel' J and Kovačičová J (1993) Review: chromatographic methods in the determination of herbicide residues in crops, food and environmental samples. *Journal of Chromatography* 643: 291

Zweig G (ed.) (1972) *Analytical Methods for Pesticides and Plant Growth Regulators*: vol. VI. *Gas Chromatographic Analysis*. New York: Academic Press.

DropBooks

Solid-Phase Extraction

Y. Picó, Universitat de València, València, Spain

Copyright © 2000 Academic Press

Solid-phase extraction (SPE) methods, using bonded-silicas, were first introduced in 1971 as an alternative to liquid partitioning. The method combines extraction and preconcentration of organic compounds in water by adsorption on proper solid material followed by desorption with a small quantity of an organic solvent. In comparison with liquid–liquid extraction, the following advantages are offered: the amount of solvent required for the clean up is greatly reduced, thus saving time for the evaporative concentration step and minimizing exposure of the analyst to the toxic solvent; the final eluate has less interfering material, and it could be analysed using any of a variety of detection, separation and identification techniques, including high performance liquid chromatography (HPLC) or gas chromatography (GC); accuracy and precision are improved; and it is rapid and easily automated.

Another impressive feature of SPE is the commercial availability of sorbents in small and inexpensive cartridges. C_{18}-bonded silica cartridges, styrene-divinylbenzene Empore® extraction discs and Carbopack® cartridges have been extensively used for the extraction of organic molecules from water samples. Automated column switching systems and on-line SPE coupled to determination devices have also been often reported for determination of pollutants in drinking and surface water.

Because of the reasons given above, in recent years much analysis of herbicides in fruit, vegetable and water has been conducted using SPE. Phenoxy acids, phenylureas, aryloxyphenoxypropionic acids, triazines, sulfonylureas, imidazolinones, glyphosate, phenoxyacetic acids, bipyridynium compounds,

chloroacetamides, dinitroanilines and substituted phenols are examples of herbicides usually extracted and isolated by this technique.

It is undeniable that SPE is gaining in importance and, today, is a well-established and validated method, since the Environmental Protection Agency (EPA) in the United States currently offers one SPE procedure for the analysis of organic compounds (including neutral herbicides) and two for the analysis of acid herbicides.

Solid-Phase Extraction

Analyte Characteristics

The determination of herbicide residues is an intricate problem because of the large number of chemicals involved. As a general rule, to classify them into a wide variety of classes depending on their chemical structure results in a lot of groups that barely provide enough information in order to select the best SPE procedure.

In this way, the most practical approach is to organize the herbicides according to their acid/base character or other properties that condition the protocol following by SPE. **Table 1** shows these characteristics for the major classes of herbicides and some examples of the structures included in each group.

Disposable Solid Phases

The modern SPE technique began in 1978 with the introduction of Sep-Pack cartridges, the first compact silica-based solid-phase extraction device for sample preparation on the market. Present-day, disposable prepacked columns or cartridges are available from more than 30 manufacturers, who offer phases such as C_{18}, C_8, cyano and amino. The containers are generally made of polypropylene. The sorbent bed varies from 100 to 1000 mg and is retained between two porous frits.

The use of Empore® discs are described in more recent studies. These devices include flat discs with large cross-sectional areas that provide advantages for preconcentration and clean-up methods with respect to the sorption, capacity, back pressure and stability after repeated use.

Reversed-phase silica-based sorbents, especially C_8 and C_{18} bonded-silicas, are the most widely used packings for SPE. A typical SPE requires a previous sorbent activation step (wetting), usually with methanol, and removal of activation solvent excess (conditioning), usually with water.

Neutral herbicides can be extracted from 1 L samples with an average amount of sorbent (500 mg). The sample is extracted under neutral or slightly alkaline conditions, and the pH is adjusted before the extraction to between 6 and 8. Under these conditions, salts of humic acids, which generally cause considerable interference in herbicide determination, are unlikely to be adsorbed during enrichment. As acid herbicides are highly polar, they are soluble in water and in aqueous solutions and are less soluble (in their dissociated form) in apolar sorbents. To overcome this difficulty, the aqueous phase has to be acidified before extraction to suppress the dissociation of this class of herbicides and to facilitate the transfer of the undissociated molecular species to the solid phase.

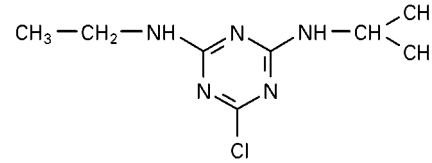
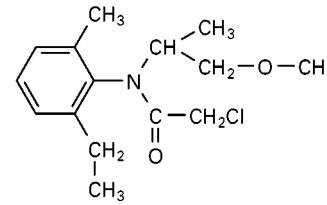
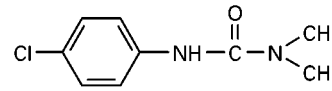
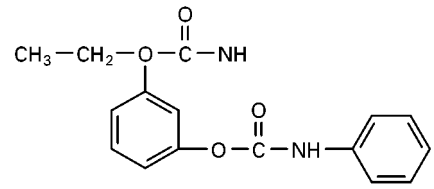
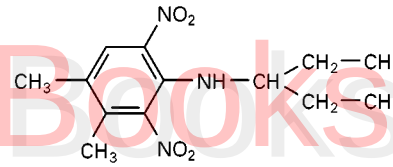
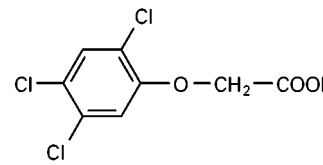
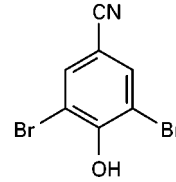
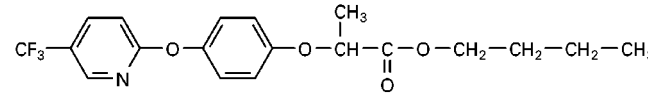
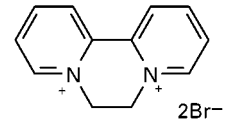
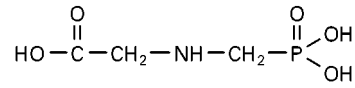
The recoveries and the relative standard deviation of the performance of different devices and solid phases are compared in **Tables 2** and **3** for basic/neutral and acid/phenolic herbicides, respectively. The C_{18} cartridges showed good recoveries with most of the basic/neutral and acidic/phenolic herbicides. Compounds having a small (deisopropylatrazine, tribensulfuron-methyl) or a very high (beta-cyfluthrine) affinity to the C_{18} material gave the worst recoveries. In comparison with Empore® discs a lower breakthrough of polar metabolites of atrazine was reported, possibly due to the fact that Empore® discs contain only half the quantity of C_{18} material. However, lower recoveries were achieved for medium polar and non-polar pesticides except trifluralin and trialate.

As reported in the literature on the subject, the bonded-silicas, in cartridge or in disc configuration, are the most commonly used supports, but they also have some limitations:

- For polar analytes, the retention is weak and often results in breakthrough during the loading step.
- Basic analytes interact strongly with the residual silanols, which in turn cause low recovery.
- The sorbent must remain wet prior to sample loading. (If one accidentally lets the cartridges run dry, the recovery is low and variable.)
- Poor stability in very acidic and basic media, which limits their use to the pH range of between 2 and 8.

These limitations have led to a search for new materials with improved characteristics. For example, the styrene-divinylbenzene resins have been extensively checked for their use in the extraction of pesticides. These polymers show higher retention of analytes and a wider pH range than C_{18} silicas. The LC-grade polymers used as stationary phases have more commonly been used in precolumns (mainly PRP-1 and PLRP-S) for on-line purposes, because

Table 1 Chemical structure of major classes of herbicides according to the character that determines the SPE procedure used

Character	*Class*	*Typical herbicide*	*Chemical structure*
Basic/neutral	Triazine	Atrazine	
	Chloroacetamide	Metolachlor	
	Urea	Monuron	
	Carbamate	Desmedifam	
	Dinitroaniline	Pendimethalin	
Acid phenolic	Phenoxy acid	2,4,5-T	
	Substituted phenol	Bromoxynil	
	Aryloxyphenoxy propanoic acid	Fluazifop	
Cationics	Bipyridilium compound	Diquat	
Very soluble	Organophosphate	Glyphosate	

DropBooks

Table 2 Relative standard deviation (RSD), recoveries (Rec.) and determination limits (DL, P 95%) for the preconcentration of basic/neutral pesticides from 1000-mL Milli-Q-water

	Concentration range (ng L^{-1})	*Preconcentration on*											
		Bond Elut C_{18} cartridges			*Empore® C_{18} discs*			*Empore® SDB discs*			*ENVI-Carb cartridges*		
		RSD (%)	*Rec. (%)*	*DL (ng L^{-1})*	*RSD (%)*	*Rec. (%)*	*DL (ng L^{-1})*	*RSD (%)*	*Rec. (%)*	*DL (ng L^{-1})*	*RSD (%)*	*Rec. (%)*	*DL (ng L^{-1})*
Desisopropylatrazine	54–270	9.9	33	133	10.6	21	143	15.9	16	221	6.9	99	96
Desethylatrazine	50–248	8.7	82	113	8.8	49	110	3.6	72	46	7.3	101	94
Metoxuron	108–538	1.9	95	58	3.4	106	95	4.8	94	134	5.7	106	159
Hexazinon	107–535	8.1	96	224	6.9	102	186	6.7	104	182	7.4	108	200
Simazine	49–245	1.5	102	20	4.5	102	57	5.2	100	66	9.3	95	117
Metribuzin	94–470	4.7	94	120	4.0	104	99	4.1	109	99	10.2	97	249
Cyanazine	57–285	7.9	81	119	5.0	110	73	6.3	93	91	5.6	82	81
Carbofuran	179–895	6.4	92	309	4.4	107	211	6.8	95	311	23.1	80	1057
Methabenzthiazuron	100–498	5.2	89	138	5.0	98	127	3.9	103	101	5.2	86	135
Chlortoluron	101–503	4.9	96	133	4.5	102	118	2.3	98	61	5.9	97	158
Atrazine	50–250	5.6	96	75	5.6	100	72	3.6	93	47	7.1	90	92
Monolinuron	149–745	4.0	96	166	13.7	105	473	5.7	114	221	7.7	89	296
Diuron	102–510	7.3	89	194	5.1	101	134	4.9	94	130	6.5	92	171
Isoproturon	109–543	6.7	90	191	5.7	102	158	7.3	95	199	6.0	100	164
Metobromuron	102–508	13.4	88	334	9.2	93	230	4.5	96	119	9.4	96	248
Metazachlor	123–165	7.3	85	235	6.5	106	204	2.2	100	72	5.3	89	177
Sebutylatrazine	53–265	4.9	97	69	4.8	103	66	4.3	102	58	4.1	97	56
Terbutylatrazine	53–263	6.3	104	87	6.6	104	89	5.7	98	77	6.2	92	83
Linuron	102–508	2.3	101	66	3.6	96	97	3.2	106	87	3.5	98	94
Napropamide	45–225	5.8	98	69	2.1	100	24	4.9	100	57	3.1	98	36
Terbuconazol	164–820	6.5	90	282	2.1	101	98	5.2	101	224	3.9	98	168
Metolachlor	127–633	3.3	103	115	6.3	100	204	7.1	104	226	5.2	89	166
Propiconazol	225–1125	4.9	96	316	2.3	99	156	4.7	107	290	6.3	97	391
Dinosebacetate	138–688	6.6	41	239	16.2	52	509	7.6	70	262	32.2	33	1108
Parathion-ethyl	148–740	4.6	90	189	8.0	101	294	7.1	97	264	6.0	88	224
Pyrazophos	125–623	7.1	82	230	3.6	93	120	5.1	107	165	32.8	38	1058
Bifenox	67–333	3.9	98	70	3.5	93	61	8.8	92	147	4.2	89	70
Prosulfocarb	140–698	4.8	91	182	11.6	94	385	5.5	72	198	6.2	66	224
Pendimethalin	121–603	8.0	84	248	9.9	93	290	4.5	107	142	10.4	62	327
Trifluoralin	125–625	8.3	63	268	14.2	21	415	0.0	0	0	10.9	60	458
Triallate	128–638	4.1	96	144	14.7	35	434	0.0	0	0	8.5	52	513
Fluoroxypyrester	81–403	3.2	86	71	5.1	89	105	6.0	98	123	8.3	52	170
Beta-cyfluthrine	190–950	3.7	61	202	8.1	82	383	2.2	89	122	15.0	42	818

(Reproduced with permission from Schülein J, Martens D, Spizauer P and Kertrup A (1995) Comparison of different solid phase extraction materials and techniques by application of multiresidue methods for the determination of pesticides in water. *Fresenius Journal of Analytical Chemistry* 352: 565–571.)

Table 3 Relative standard deviation (RSD), recoveries (Rec.) and determination limits (DL, P 95%) for the preconcentration of acidic phenolic pesticides from 1000-mL Milli-Q-water

	Concentration range (ng L^{-1})	*Preconcentration on*											
		Bond Elut C_{18} cartridges			*Empore® C_{18} discs*			*Empore-SDB discs*			*ENVI-Carb cartridges*		
		RSD (%)	*Rec. (%)*	*DL (ng L^{-1})*	*RSD (%)*	*Rec. (%)*	*DL (ng L^{-1})*	*RSD (%)*	*Rec. (%)*	*DL (ng L^{-1})*	*RSD (%)*	*Rec. (%)*	*DL (ng L^{-1})*
Trifensulfuron-methyl	52–258	5.3	38	71	7.4	93	99	5.2	68	67	5.3	76	69
Metsulfuron-methyl	53–263	6.7	43	92	4.8	85	66	5.0	71	66	9.5	77	126
Dicamba	91–464	3.9	63	96	3.8	46	93	4.9	115	116	6.5	97	153
MCPA	96–487	8.5	98	208	6.5	99	164	12.8	59	300	10.7	124	252
Bromoxynil	110–561	3.9	76	119	6.1	65	177	3.8	67	111	7.1	89	206
Dichlorprop	105–533	4.1	99	118	4.2	94	119	3.0	83	84	2.4	104	67
Ioxynil	88–446	6.6	100	151	4.7	95	110	6.3	76	140	7.0	91	156
MCPB	91–464	8.7	88	202	5.0	94	121	9.9	106	220	3.6	88	80
Bifenox acid	70–357	5.6	88	104	4.5	103	85	4.4	97	80	3.8	96	69
Haloxyfop	104–528	6.1	100	166	4.3	99	121	4.7	104	127	4.2	91	113

(Reproduced with permission from Schülein J, Martens D, Spizauer P and Kertrup A (1995) Comparison of different solid phase extraction materials and techniques by application of multiresidue methods for the determination of pesticides in water. *Fresenius Journal of Analytical Chemistry* 352: 565–571.)

they are too expensive for use in disposable SPE cartridges. Empore® extraction discs have recently become available, with styrene divinylbenzene (SDB) copolymer sorbents enmeshed in the matrix.

Recoveries of acid herbicides from water samples have been compared by using C_{18} and SDB discs; the results of this comparison are controversial. Some authors documented an improvement in the recoveries of phenoxycarboxylic acid and phenols on SDB discs for the enrichment of samples down to 500 mL (see **Table 4**). The addition of salt considerably enhances the recovery and decreases the differences between the extraction efficiency of C_{18} and resin discs. However, other authors reported that SDB discs showed worse recovery rates under acidic conditions, in comparison with C_{18} when preconcentrations were carried out with 1-L samples (see Table 3). In any case, salting out the water sample enhances the retention of substances on both materials; this increases recovery rates for hydrophilic substances. However, salting out is avoided as it may introduce impurities into the samples. The addition of a small quantity of methanol or other organic solvent also enhances the recovery by the so-called 'dynamic solvation'. However, it is not recommended, as it produces a relatively early breakthrough of hydrophilic substances.

Graphitized carbon black (GCB) has been confirmed to be a valuable adsorbing material for SPE of pesticides in aqueous environmental samples. GBC cartridges proved to be more efficient than the more commonly used C_{18} bonded-silica cartridges for the SPE of polar herbicides, whereas the extraction of non-polar compounds showed inferior results (see Table 3). Although GCB is known to behave as a natural reversed phase, it contains chemical heterogeneities on its surface, which are able to bind anions via electrostatic forces. GBC can behave as both a reversed-phase sorbent and an anion exchanger, retaining the acidic pesticides in their ionic form under acidic conditions. In this situation, the base–neutral/acid fractionation can be achieved by using solvent mixtures at different pHs.

Silica-based ion exchangers are found in disposable SPE cartridges. They are not widely used for the preconcentration of environmental samples owing to their low capacity. Strong anion exchanger discs have been used for the analysis of chlorinated acid and phenoxy acid herbicides. The main problem with these comes from the fact that environmental waters contain high amounts of inorganic ions, which overload the capacity of the sorbent.

Selective SPE from environmental waters has been accomplished by using different sorbents coupled in the same or in different cartridges.

DropBooks

Table 4 C_{18} and resin recoveries and effect of salting water

Analyte	*Recoveries ± RSD (%; n = 3)*			
	C_{18}[1]	*Resin[1]*	*C_{18}[2]*	*Resin[2]*
Acifluorfen	77 ± 20	82 ± 5	104 ± 5	121 ± 1
Bentazon	0	ND	90 ± 13	71 ± 5
Chloramben	8 ± 11	3 ± 15	72 ± 14	77 ± 7
2,4-D	86 ± 12	83 ± 6	81 ± 8	94 ± 15
Dalapon	0	42 ± 25	12 ± 75	31 ± 30
2,4-DB	81 ± 13	80 ± 14	118 ± 10	130 ± 8
Dacthal	53 ± 17	99 ± 8	67 ± 16	97 ± 5
Dicamba	73 ± 13	71 ± 14	83 ± 3	94 ± 15
3,5-Dichlorobenzoic acid	70 ± 17	76 ± 2	86 ± 25	107 ± 20
Dichloroprop	77 ± 11	78 ± 3	85 ± 9	94 ± 10
Dinoseb	72 ± 16	75 ± 5	92 ± 26	85 ± 6
Pentachlorophenol	69 ± 14	70 ± 2	65 ± 15	73 ± 8
Pichloram	49 ± 19	74 ± 7	96 ± 24	99 ± 21
2,4,5-T	76 ± 11	75 ± 14	93 ± 10	89 ± 5
Silvex	73 ± 14	74 ± 14	82 ± 9	80 ± 5

[1]Fortified, unsalted reagent water.
[2]Fortified reagent water with 20% (w/w) Na_2SO_4.
ND, no data.
(Reproduced with permission from Hodgeson J, Collins J and Bashe W (1994) Determination of acid herbicides in aqueous samples by liquid–solid disk extraction and capillary gas chromatography. *Journal of Chromatography A* 659: 395–401.)

One of the sorbents is non-specific, such as GCB, which traps the analytes of interest and many other compounds, while the other is more specific, such as a cation or anion exchanger, which retains and reconcentrates the analytes of interest. **Table 5** shows the recoveries of nine phenoxy acid herbicides extracted by one miniaturized cartridge containing 50 mg of GCB at the top and 70 mg of a silica-based strong anion exchanger (SAX) at the bottom, compared with C_{18} and anion exchanger extraction. A large loss of dicamba and incomplete recovery of phenoxyacids were obtained by using the resin-based exchanger material.

Ammonium quaternary compounds and glyphosate constitute a special and complicated case. Their determination is very important because they are among the top herbicides used in the world. An important drawback in the preconcentration of such compounds from water is their high polarity. Several efforts have been made to analyse them in environmental samples.

SPE of ammonium quaternary herbicides has been mainly performed with silica, which is a well-known example of the solid phase using adsorption and ionic interaction mechanisms with the silanol groups. Recoveries are rather acceptable in the pH range 7.5–9. Taking into account that at pH values higher than 7 the silanol groups of the stationary phase are ionized, at these pH values the cation-exchange capacity of the solid-phase will be increased.

Glyphosate, due to its ionic form, can be preconcentrated using anionic and cationic resins. Derivatization of the analyte, prior to SPE of the water sample, seems to help the concentration from water samples.

Table 5 Recovery of herbicides from 200-mL groundwater samples by using one cartridge containing GCB and anion exchanger compared with that from two other extraction methods

	% Recovery[1]			
	C_{18}		*Anion exchanger*	*GCB + anion exchanger*
	pH 2	*pH 7.9*		
Dicamba	94.2	< 10	23.0	97.3
2,4-D	96.1	< 10	78.3	98.4
MCPA	96.4	< 10	77.7	97.6
2,4-DP	97.7	< 10	76.8	96.4
MCPP	94.4	< 10	82.0	97.3
2,4,5-T	93.5	< 10	81.4	95.4
2,4-DB	96.0	< 10	82.3	98.9
MCPB	95.8	< 10	81.5	96.5
2,4,5-T	93.1	< 10	77.3	95.2

[1]Mean values were calculated for two determinations.
(Reproduced with permision from Di Corcia A, Marchetti M and Sampieri R (1989) Extraction and isolation of phenoxyacid herbicides in environmental waters using two adsorbents in one minicartridge. *Analytical Chemistry* 61: 1363–1367.)

Table 6 Desorption efficiencies from the solid phase and overall recoveries of herbicides

Herbicide	*Desorption efficiency (%)*										*Recovery from filtered river water (%)*[5]	
	Methanol		*Ethyl acetate*		*Acetone (3 mL)*		*Acetone*		*Acetone (6 mL)*			
	3 mL	*6 mL*	*3 mL*	*6 mL*	*Mean*[1]	*RSD*[2]	*3 mL + HX*[3]	*3 mL + DCM*[4]	*Mean*[1]	*RSD*[2]	*Mean*[1]	*RSD*[2]
ACN	68.9	68.9	78.3	78.3	74.6	8.4	74.6	74.6	81.9	12	128	14
Alachlor	67.7	67.7	80.5	80.5	80.1	7.4	80.1	80.1	101	6.1	105	3.4
Benfluralin	48.1	48.1	73.4	73.4	55.0	13	69.6	70.3	67.9	1.8	83.6	2.2
Bifenox	< 5	< 5	78.3	78.3	69.2	9.1	69.2	79.0	92.9	8.2	98.1	5.7
Bromobutide	77.1	77.1	78.2	78.2	80.1	8.5	80.1	80.1	103	2.7	108	3.9
Bromobutide-debromo	76.4	76.4	76.6	76.6	79.5	7.8	79.5	79.5	92.7	7.8	101	7.1
Butachlor	50.6	64.0	79.6	79.6	73.4	9.3	83.5	83.1	100	5.2	112	1.1
Butamifos	73.9	73.9	81.4	81.4	81.2	9.2	81.2	81.2	96.5	3.9	104	2.6
Chlomethoxyfen	< 5	< 5	74.9	74.9	70.9	5.9	70.9	83.2	91.3	8.7	97.9	6.7
Chlornitrofen	< 5	< 5	77.8	77.8	63.2	13	70.6	80.5	71.9	3.2	81.6	4.4
Chlorprofam	57.5	57.5	81.1	81.1	68.2	5.1	68.2	79.1	95.7	5.4	103	4.6
Dimepiperate	< 5	42.2	80.1	80.1	71.7	7.8	84.0	85.8	104	8.9	110	4.8
Dimethametryn	64.5	64.5	83.1	83.1	79.4	6.9	79.4	79.4	96.4	3.2	105	5.8
Dithiopyr	73.5	73.5	79.5	79.5	74.4	6.6	74.4	82.4	84.1	8.6	85.9	5.0
Esprocarb	< 5	35.9	76.2	76.2	63.4	13	77.5	78.3	87.3	3.6	94.1	0.23
MCPA-ethyl	22.5	47.3	72.6	72.6	57.9	12	70.3	74.8	89.7	5.8	89.3	5.3
MCPA-thioethyl	< 5	< 5	76.6	76.6	57.9	14	74.8	82.6	98.1	4.0	98.9	6.5
Mefenacet	< 5	55.4	78.2	78.2	82.5	2.5	82.5	82.5	90.7	2.9	103	12
Molinate	25.8	45.9	76.8	76.8	64.1	9.7	75.9	80.5	90.8	7.0	98.7	6.2
Naproanilide	< 5	60.0	76.8	76.8	79.8	2.4	79.8	79.8	96.0	3.1	103	9.5
Oxadiazon	38.0	59.4	76.1	76.1	70.8	6.7	83.2	84.0	93.2	1.8	96.8	1.6
Pendimethalin	< 5	42.9	92.6	92.6	71.1	8.9	86.4	86.5	73.2	7.3	86.4	2.8
Piperophos	54.1	71.8	79.9	79.9	85.9	5.7	85.9	85.9	93.5	5.3	100	9.1
Pretilachlor	64.1	64.1	78.5	78.5	79.8	8.6	79.8	79.8	108	6.5	112	2.7
Prometryn	70.9	70.9	79.4	79.4	82.8	8.2	82.8	82.8	93.6	4.5	101	4.1
Simazine	84.6	84.6	78.1	78.1	78.9	11	78.9	78.9	102	9.6	112	7.3
Simetryn	78.8	78.8	77.9	77.9	80.4	9.2	80.4	80.4	93.5	9.4	120	11
Thiobencarb	< 5	30.7	80.3	80.3	64.4	13	77.6	80.6	97.6	5.1	110	0.63
Trifluralin	50.3	50.3	76.8	76.8	57.3	13	71.1	72.3	72.1	1.2	87.1	5.8

[1]Percentage mean recovery ($n = 3$).
[2]Percentage relative standard deviation.
[3]A 3-mL volume of hexane.
[4]A 3-mL volume of dichloromethane.
[5]The herbicides collected on the cartridges were eluted with 6 mL of acetone.
(Reproduced with permission from Tanabe A, Mitobe H, Kawata K and Sakai M (1996) Monitoring of herbicides in river water by gas chromatography–mass spectrometry and solid phase extraction. *Journal of Chromatography A* 754: 159–168.)

CRC PRESS BOOKS

It can be concluded that C_{18} material is inappropriate for some herbicides, especially more polar and very non-polar herbicides. In these cases, the SDB polymers and GCB offer a valuable alternative. The appropriate choice of solid phase for application to a separation problem will vary from case to case and must be adapted accordingly.

Elution of the Target Analytes

Desorption of the compounds from the concentration columns is mainly performed with a small volume of liquid. The partition coefficient in a given solid-phase eluent system should favour the shift of the studied herbicides. On the other hand, SPE is not a separate step, but it is part of a process that includes subsequent determination and so it should be taken into account that some determination systems, such as GC, are incompatible with the presence of water. In this way, the selection of the eluting solvent depends on the selected sorbent, the analytes and the detection method. Air-drying is often applied before analyte elution in order to remove residual water.

Methanol and acetonitrile are recommended solvents for the elution of herbicides adsorbed to C_8 or C_{18} silicas. Dichloromethane and ethyl acetate have also been extensively used, especially when the presence of water is undesirable. **Table 6** presents the results obtained when herbicides were eluted from a cartridge using different solvents, such as methanol, ethyl acetate, acetone, hexane and dichloromethane following acetone.

Desorption of acid herbicides from the sorbents can also be performed using a solution adjusted to a pH where the analytes are in their ionic form (two units below or above the pK_a). The uniqueness of GCB is that acid compounds are retained in their ionic forms and neutral compounds are adsorbed by unspecific mechanisms. In this situation, base–neutral/acid fractionation can be easily achieved by first eluting base–neutral species with a neutral organic solvent mixture and then passing a basified or acidified solvent system to desorb acidic compounds. **Table 7** reports the results obtained using base–neutral/acid fractionation in three kinds of GCB. In all cases, there was some carryover of 2,4-DB, which is the weakest compound included in this table.

With ion exchange sorbents, the analytes can be eluted from the SPE column by either adjusting the pH in order to neutralize the charge on the analyte or by using a buffer of high ionic strength.

Sample Requirements

Samples undergoing SPE need to be filtered to separate suspended matter. Filtration is especially necessary before extraction of surface water, but is also

Table 7 Base–neutral/acid fractionation by differential elution of selected compounds with cartridges containing three different types of GCB at two eluents

Compound	*Sorbent material*					
	Carbograph 1		*Carbograph 4*		*Carbograph 5*	
	Eluent A[1]	*Eluent B*[3]	*Eluent A*	*Eluent B*	*Eluent A*	*Eluent B*
Base/neutral						
Atrazine	97	—	95	—	94	—
Linuron	99	—	98	—	95	—
Aldicarb	92	—	92	—	92	—
Acidic						
Dichlorprop (3.5)[3]	—	95	—	97	30	73
2,4,5-T (2.2)	—	97	—	102	—	99
Ioxynil (3.9)	—	101	—	102	—	93
2,4-D (2.6)	—	99	—	100	—	93
2,4-DB (4.8)	40	63	18	81	50	49
Mecoprop (3.7)	—	99	—	99	—	96

Extraction from 1 L of Aldrich humic acid-spiked drinking water (spiked level, 10 $\mu g\ L^{-1}$). Mean recovery values obtained from three measurements.

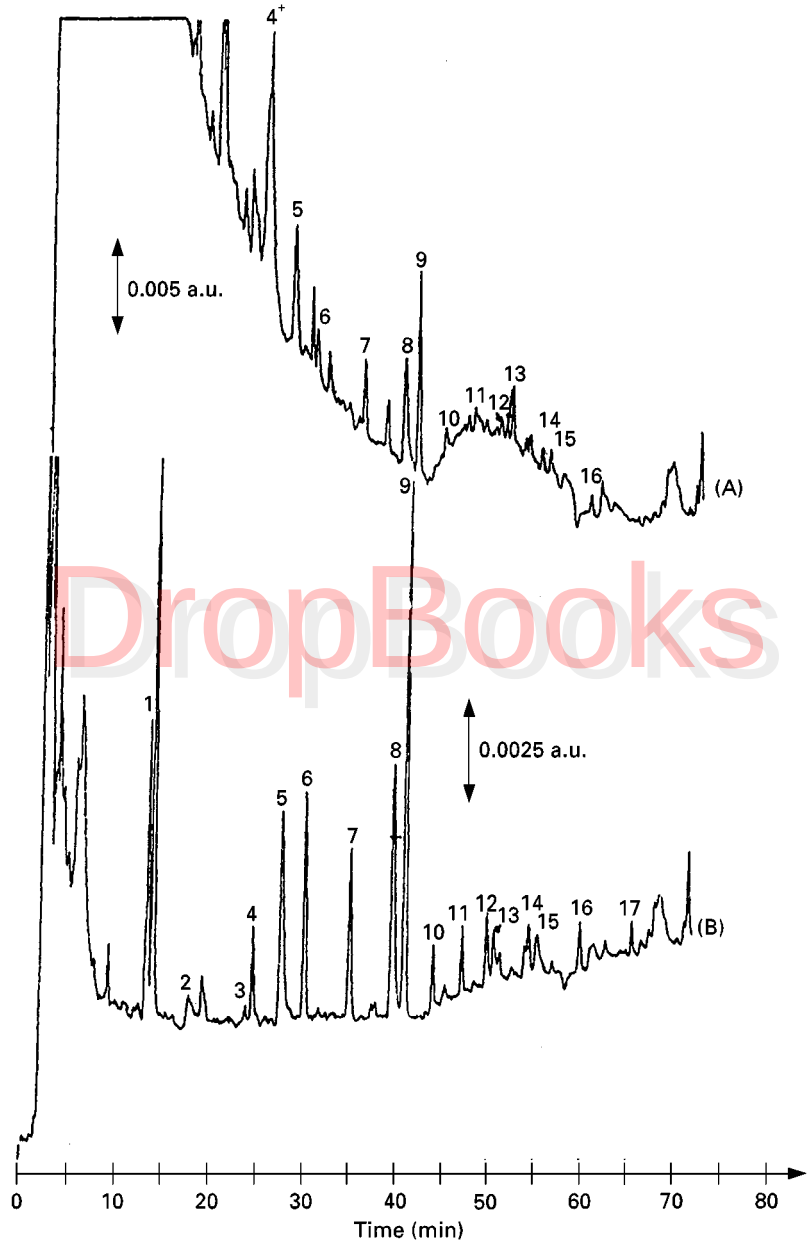
[1]Eluent phase: CH_2Cl_2–CH_3OH (80 : 20).

[2]Eluent phase: CH_2Cl_2–CH_3OH (80 : 20) + 10 mmol L^{-1} tetrabutylammonium chloride (TBACI).

[3]Reported pK_a values of the acidic compounds are given in parentheses.

(Reproduced with permission from Crescenzi C, Di Corcia A, Passariello G, Samperi R and Turnes MI (1996) Evaluation of two new examples of graphitized carbon blacks for use in solid-phase extraction cartridges. *Journal of Chromatography A* 733: 41–55.)

often advisable for extraction of ground water to avoid blocking up the cartridge material. However, waters from different sources are very different in chemical composition. Matrix effects from the water itself can cause errors in quantitation and determination. The presence in waters of common contaminants (natural or xenobiotics), such as humic acids, surfactants, inorganic salts, phenols, polycyclic aromatic hydrocarbons (PAH), other pesticides and related compounds, can negatively affect the analysis, significantly diminishing the recovery efficacy or interfering with the posterior determination. **Figure 1** shows that when natural samples are acidified, humic and fulvic acids are



DropBooks

Figure 1 Effect of the pH of the sample on the preconcentration of 500 mL of drinking water spiked at 0.1 μg L^{-1}. Sample (A) adjusted to pH 3 with perchloric acid and (B) not adjusted (pH 7). Analytical conditions: flow-rate, 1 mL min^{-1}, loop, 50 μL; mobile phase, acetonitrile gradient with 0.005 M phosphate buffer acidified to pH 3 with $HClO_4$, gradient from 10 to 30% acetonitrile from 0 to 10 min, and from 30 to 77% from 10 to 80 min; UV detection at 220 nm. Peaks: 1, chloridazon; 2, dicamba; 3, aldicarb; 4, methoxuron; 5, simazine; 6, cyanazine; 7, bentazone; 8, atrazine; 9, carbaryl; 10, isoproturon; 11, ioxynil; 12, MCPP; 13, difenoxuron; 14, 2,4-DB; 15, 2,4,5-T; 16, metolaclor; 17, dinoterb. (Reproduced with permission from Pichon V, Cau Dit Coumes C, Chen L, Guenu S and Henion MC (1996) Simple removal of humic and fulvic acid interferences using polymeric sorbents for the simultaneous solid-phase extraction of polar acidic, neutral and basic pesticides. *Journal of Chromatography A* 737: 25–33.)

Table 8 Recoveries of cationic herbicides (4 μg L^{-1}) from 0.25 L of water samples containing various concentrations of different surfactants

Surfactants	*Concentration (μg L^{-1})*	*Recovery (%)*[1]		
		Diquat	*Paraquat*	*Difenzoquat*
Cetrimide	5	98	99	90
	50	93	92	92
	300	95	91	93
	3000	87	89	92
Benzalkonium chloride	5	114	114	94
	50	107	107	93
	300	102	102	95
	3000	105	105	103
Sodium tetradecyl sulfate	5	99	102	87
	50	98	95	93
	300	41	47	41
	3000	34	30	37
Lauryl sulfate	5	84	85	92
	50	109	100	93
	300	42	35	41
	3000	34	30	39
Laurylsulfobetaine	5	89	83	79
	50	91	94	84
	300	47	57	42
	3000	54	55	48
Brij-35	5	85	89	92
	50	83	101	91
	300	45	33	37
	3000	36	30	42
Triton X-100	5	86	89	92
	50	102	101	91
	300	45	33	37
	3000	36	30	42

[1]Average recovery calculated from four determinations.
(Reproduced with permission from Ibáñez M, Picó Y and Mañes J (1996) Influence of organic matter and surfactants on solid-phase extraction of diqua, paraquat and difenzoquat from waters. *Journal of Chromatography A* 727: 245–252.)

co-extracted and co-eluted, which generates a large, unresolved peak in the chromatogram when HPLC with UV detection is used (chromatogram A). At pH 7, humic and fulvic acids are not co-extracted, as can be seen by the flat baseline from the beginning to the end of chromatogram (B).

Organic matter and anionic or non-ionic surfactants have demonstrated negative effect on the recovery of any class of herbicides. Although these undesirable effects are well known, only a few analytical studies have focused on ways in which to avoid them. The proposed methods for removing interferences are based on the use of chemical reagents, such as sulfite or cationic surfactants. In these cases, the recovery values after chemical treatment were similar to those when a Milli-Q-quality water standard was analysed. The recoveries reported in **Table 8** show that the quantitative SPE of diquat, paraquat and difenzoquat is affected by the presence of anionic, zwitterionic and non-ionic surfactants when they are present in water at a level of up to 50 μg L^{-1}.

Although some common contaminants of natural waters have a negative effect on the recoveries, SPE is useful for analysing herbicides in drinking and surface water because only in very extreme conditions does the concentration of these contaminants reach levels at which recoveries are significantly decreased.

The application of SPE to the isolation of herbicide residues from other matrices presents difficulties that must be overcome, which have, up to now, discouraged investigation into the use of other matrices. For liquid matrices (plasma, urine, blood or milk), acceptable recoveries have been obtained using protein precipitation prior to SPE but the impurities present can accumulate in the analytical columns and affect the chromatogram. The recoveries obtained by SPE for determining triazines from milk are compared with those obtained by liquid–liquid extraction (Hajšlova *et al.*) in **Table 9**. SPE was performed using a double trap: first, a non-specific adsorbent (GCB), and then a cation exchanger. The liquid–liquid extraction method, after an initial double protein precipitation using methanol in

Table 9 Recovery ($n = 6$) of triazines from fortified (50 ng mL^{-1}) skimmed milk using the proposed method and that of Hajšlovà *et al.*

Compounds	*Recovery % (mean ± RSD)*	
	SPE method	*Hajšlovà et al.*
Simazine	89.7 ± 4.1	86.1 ± 5.2
Atrazine	89.3 ± 3.9	84.3 ± 4.7
Prometon	90.4 ± 4.0	92.4 ± 4.3
Ametryn	89.5 ± 3.5	90.0 ± 4.7
Propazine	93.4 ± 3.6	88.6 ± 4.2
Terbutylazine	91.6 ± 3.4	87.3 ± 4.2
Prometryn	87.2 ± 3.8	85.5 ± 4.0
Terbutryn	77.8 ± 3.2	80.9 ± 3.9

(Reproduced with permission from Lagana A, Marino A and Fago C (1995) Evaluation of double solid-phase extraction system for determining triazine herbicides in milk. *Chromatographia* 41: 178–182.)

basic and acid environments, used a partition with chloroform followed by a sample clean up using a silica cartridge. There were no significant differences in the triazine recovery using the two methods.

Solid matrices can also be extracted by SPE with cartridge or disc devices but require a separate homogenization step and other laborious processes. The reported recoveries are lower than those obtained with water, and the addition of methanol or acetonitrile as organic modifier is necessary. However, these recoveries are comparable to those obtained by other well known extraction methods for solid matrices. **Table 10** gives a comparison of the features of three extraction procedures for tribenuron methyl analysis in soil. Solid-phase and supercritical fluid extractions are the most adequate in terms of recovery percentage and precision, with acceptable detection limits; nevertheless, the recovery is affected by the amount of herbicide present in soil. SPE can also be performed by blending directly a homogenized sample with C_{18} sorbent, transferring the mixture to a glass chromatography column and eluting the analytes with appropriate solvent.

The SPE of matrices other than water requires further investigation.

On-line and Off-line Procedures

Nowadays, SPE methods using off-line procedures can be converted into on-line SPE methods by direct connection of the precolumn to the analytical column via switching valves. The concentrated analytes are then directly desorbed and transferred to the analytical system. Such systems often involve microprocessor control of the stages for sample switching and flushing of solvents and eluents through the concentration and chromatographic columns.

On-line procedures have gained popularity since European Union (EU) guidelines were introduced which limited the maximum amount allowed for a single pesticide in drinking water to 0.1 μg L^{-1} and for several pesticides to 0.5 μg L^{-1}, including toxic transformation products. Very sensitive methods are required for monitoring herbicide residues in drinking water at such low concentrations. Furthermore the recent commercialization of automatic devices has certainly helped in the development of on-line trace enrichment methods in environmental analysis, because the sequence can be totally automated using systems such as the Prospect module (Spark Holland) or the OSP-2 system (Merck).

On-line SPE-LC is the most common procedure used because it is easily performed in any laboratory. The extracted compounds are eluted directly from the precolumn to the analytical column by a suitable mobile phase, which permits the separation of the trapped compounds. It is well established that on-line procedures enable lower concentrations of pesticides to be determined, and most compounds can be kept within EU limits. **Table 11** illustrates the improvement in detection limits obtained for triazine and phenylurea herbicides using on-line procedures when compared with off-line ones.

Breakthrough is the key parameter in on-line SPE because it indicates the sample volume and the amount of analyte that can be preconcentrated. Two factors can be responsible for breakthrough: insufficient retention of the analytes by the sorbent and overloading of the sorbent. One important factor of the concentration procedure is the selection of the

DropBooks

Table 10 Comparison of the extraction procedures for tribenuron methyl analysis

Extraction	*Efficacy*	*Precision*	*Selectivity*	*Operation time*	*Affecting factors*	*Detection limit*
Solvent	+	+ +	+ + +	+ +	No data	No data
Solid-phase	+ +	+ + +	+ + +	+ +	Concentration	+ + +
Supercritical fluid	+ +	+ + +	+ + +	+ + +	Concentration	+ + +

+, Bad; + +, regular; + + +, good.
(Reproduced with permission from Berna JL, Jiménez JJ, Herguedas A and Atienza J (1997) Determination of chlorsulfuron and tribenuron-methyl residues in agricultural soils. *Journal of Chromatography A* 778: 119–125.)

Table 11 Range of linearity, r^2 and detection limit (LOD) for the on-line method

Pesticide	*Off-line method*			*On-line method*		
	Range of linearity ($\mu g\ L^{-1}$)	*r^2*	*LOD ($\mu g\ L^{-1}$)*	*Range of linearity ($\mu g\ L^{-1}$)*	*r^2*	*LOD ($\mu g\ L^{-1}$)*
Simazine	0.5–50	0.9985	0.1	0.1–8	0.9990	0.03
Cyanazine	0.5–50	0.9973	0.1	0.1–8	0.9987	0.03
Chlortoluron	0.5–50	0.9960	0.1	0.2–8	0.9956	0.05
Atrazine	0.5–50	0.9980	0.1	0.1–8	0.9999	0.03
Isoproturon	1.0–50	0.9990	0.1	0.2–8	0.9993	0.05
Ametryn	0.5–50	0.9985	0.05	0.1–8	0.9993	0.03
Prometryn	0.5–50	0.9989	0.05	0.1–8	0.9995	0.03
Terbutryn	0.5–50	0.9980	0.05	0.1–8	0.9985	0.03
Chlorpyriphos-methyl	2.0–50	0.9962	0.5	0.5–8	0.9980	0.20
Fenitrothion	2.0–50	0.9983	0.5	0.5–8	0.9993	0.20
Fenchlorphos	5.0–50	0.9950	1.0	1.0–8	0.9927	0.30
Parathion-ethyl	5.0–50	0.9944	1.0	1.0–8	0.9995	0.30

(Reproduced with permission from Aguilar C, Borrull F and Marcé RM (1996) On-line and off-line solid-phase extraction with styrene-divenylbenzene-membrane extraction disks for determining pesticides in water by reversed-phase liquid-chromatography-diode array detection. *Journal of Chromatography A* 754: 77–84)

sorbent, which must allow a convenient breakthrough of the analytes. **Table 12** shows a comparison of SPE sorbents for analysis of phenyl carbamate herbicides. The results were unsatisfactory with some herbicides. GCB is not used much in online SPE because it is not sufficiently pressureresistant.

Another factor in the procedure is to evaluate the maximum sample volume that can be preconcentrated without breakthrough of analytes, thus avoiding peak broadening. Generally, 50 mL was considered as optimum, but it could be increased for a particular kind of herbicide.

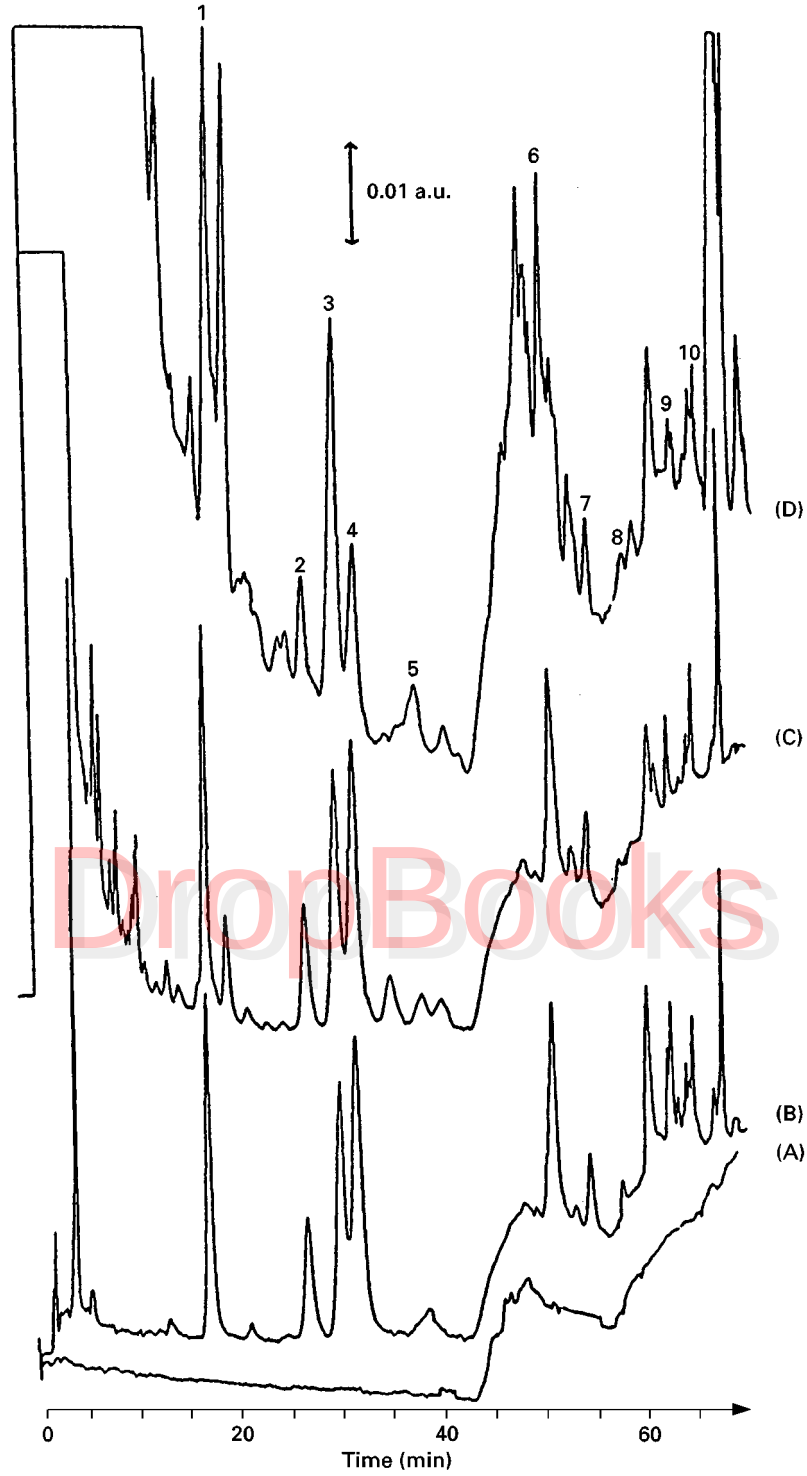
It should be taken into account that sorbents used in on-line SPE are not selective and numerous compounds from the matrix of natural samples are preconcentrated and can be eluted with the analytes of interest. Interferences depend on the nature of the water. They have an effect on both detection limits and quantification. **Figure 2** shows some chromatograms obtained with different waters. In spite of the presence of interference peaks, it can be seen that making a good choice of preconcentration parameter and analytical conditions, allows low levels of many pesticides to be determined, even in highly contaminated surface waters.

In this way, the EPA in the United States currently offers an on-line SPE procedure followed by HPLC for the analysis of acidic herbicides in drinking water. The sample is first adjusted to pH 12 to hydrolyse esterified analytes, then it is acidified to a pH of 1 and a 20-mL aliquot is pumped through a reversed-phase concentration column. By use of a switching valve, the concentration column is then pumped in line with the analytical column and the sample constituents are then passed to the analytical column for separation and detection.

Table 12 Average recoveries and RSDs (%) of the analytes by the proposed on-line SPE-LC-DAD procedures in environmental water samples spiked at different levels

Compound	*C_{18} pre-column*				*PRP-1 pre-column*			
	Drinking water		*Surface water*		*Drinking water*		*Surface water*	
	0.5 $\mu g\ L^{-1}$	*4 $\mu g\ L^{-1}$*	*0.5 $\mu g\ L^{-1}$*	*4 $\mu g\ L^{-1}$*	*0.2 $\mu g\ L^{-1}$*	*1 $\mu g\ L^{-1}$*	*0.2 $\mu g\ L^{-1}$*	*1 $\mu g\ L^{-1}$*
Carbetamide	—	105 (3)	—	105 (4)	84 (12)	101 (3)	102 (8)	101 (3)
Propham	101 (2)	98 (3)	99 (3)	97 (3)	90 (5)	102 (5)	97 (6)	102 (3)
Desmedipham	84 (9)	86 (8)	94 (7)	98 (7)	—	—	—	—
Phenmedipham	87 (2)	97 (6)	98 (10)	108 (7)	87 (3)	101 (2)	93 (6)	104 (3)
Chlorbufam	105 (5)	99 (2)	102 (4)	97 (1)	106 (7)	101 (3)	99 (5)	105 (2)
Chlorpropham	103 (2)	99 (1)	108 (3)	106 (2)	105 (5)	101 (4)	99 (5)	108 (2)

(Reproduced with permission from Hidalgo C, Sancho JV, López FJ, and Hernández F (1998) Automated determination of phenylcarbamate herbicides in environmental water by on-line trace enrichment and reversed-phase liquid chromatography-diode array detection. *Journal of Chromatography A* 823: 121–128.)



DropBooks

Figure 2 On-line analysis of 150 mL of different water samples spiked with 0.3 μg L^{-1} of (1) simazine, (2) methabenzthiazuron, (3) atrazine, (4) carbaryl, (5) isoproturon, (6) propanil, (7) linuron, (8) fenamiphos, (9) fenitrothion and (10) parathion. Precolumn, PRLP-S. (A) Blank gradient; (B) Milli-Q-purified water; (C) drinking water; (D) surface water from the Seine (28 June 1993). (Reproduced with permission from Pichon V and Henion MC (1994) Determination of pesticides in environmental water by automated on-line trace-enrichment and liquid chromatography. *Journal of Chromatography A* 665: 269–281.)

On-line SPE-GC is another interesting approach that has gained popularity over the last few years. The SPE-GC coupled techniques generally use an uncoated, deactivated capillary precolumn, also known as a retention gap, which accommodates the liquid SPE eluent while it vaporizes, thereby providing

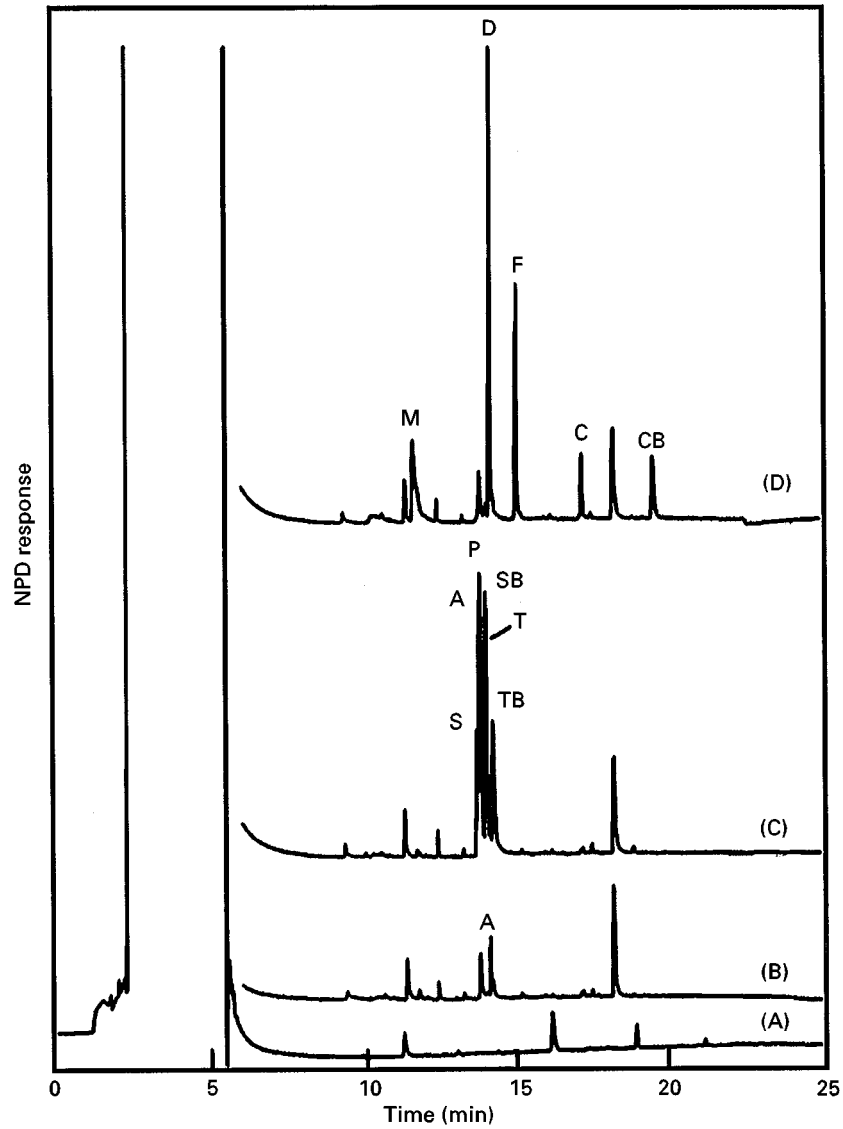


Figure 3 SPE-GC-NPD chromatograms obtained after preconcentration of 10 mL of (A) HPLC grade water, (B) Amsterdam drinking water, and drinking water spiked with (C) triazines (0.1 $\mu g\ L^{-1}$) and (D) OPPs (0.03 $\mu g\ L^{-1}$). Peak assignment for the herbicides: S, simazine; A, atrazine; P, propazine; SB, secbumeton; T, trietazine; and TB, terbutylazine. GC programme: 75°C during sample introduction, then to 300°C at 15°C min^{-1}; held at 300°C for 5 min. (Reproduced with permission from Picó Y, Louter AJH, Vreuls JJ and Brinkman UATh (1994) On-line trace-level enrichment gas chromatography of triazine herbicides, organophosphorus pesticides, and organosulfur compounds from drinking and surface waters. *Analyst* 119: 2025–2031.)

solute preconcentration. **Figure 3** shows typical results for the SPE-GC-nitrogen phosphorus detector (NPD) analysis of triazines. The most striking observation is the good baseline stability, because NPD is a very selective detector. The drawback of this technique is the high cost involved, which makes it unaffordable by most of the laboratories involved in herbicide analysis.

The analysis of herbicides, using an automated on-line solid-phase extraction device results in:

- a reduction in error
- a more efficient use of time
- savings in amount of solvent used
- an improved chromatographic separation
- a reduction of sample volume needed to achieve good results (up to 200 mL)
- a ten-fold improvement detection limit over that required by EPA and EU regulations (limit values)

The advantages cited for on-line procedures are convenient for some analysts, but many prefer the off-line approach, which gives a convenient extract in an organic solvent suitable for multiple analyses. Moreover, such an extract is generally much more stable than the aqueous sample from which it

was derived, and is therefore more suitable for long-term storage. Also, the off-line approach allows the processing of many samples at one time, an approach which is generally more productive in laboratories that are not fully automated.

Both off-line and on-line techniques are not mutually exclusive. The possibility of employing both methods gives the analyst more tools at his/her disposal for performing the analysis adequately.

Future Developments

Today, SPE has become generally accepted as the analytical method of choice for determination of all major herbicide groups in water. It is suitable for detecting approximately 300 pesticides and pesticide-related compounds and has undergone rigorous multi-laboratory calibration studies. SPE is also the backbone of residue analysis protocols for government agencies such as the EPA in the US. However, there is still much to be done. The development of new, more selective supports for SPE, its coupling with high separation power techniques, such as capillary electrophoresis (CE), and its application to extract herbicide residues from solid samples, may further reduce the detection limit and will represent an exciting challenge for researchers working in the area of herbicide residue analysis.

Looking to the future, it is interesting to note that new SPE sorbents involving antigen–antibody interaction, so-called immunosorbents, have been described. Due to their high affinity and high selectivity for these interactions, extraction and clean up of complex aqueous environmental samples is achieved in the same step. Their application to extracts from solid samples is solvent-free and simpler than any other clean-up procedure. Two class-selective immunosorbents have been optimized up to now that enable the trapping of two groups of widely used herbicides, phenyl urea and triazines.

Experiments have been recently designed to explore the possibility of recovering herbicide residues from food, soil, biological liquid and tissue samples by SPE. For liquid matrices, such as plasma, urine, fruit juice or milk, acceptable residue recovery may be obtained almost without clean up. Before SPE can be used with solid matrices (e.g. muscle, vegetables or soil) a separate homogenization step and often multiple filtration, sonication and centrifugation are required. Despite these drawbacks, SPE has been used a few times to extract residues of triazines, carbamates, ureas and other herbicides. More work is needed to further develop SPE for use with the many different types of matrices that may contain herbicide residues.

Capillary electrophoresis (CE) is very much suited for those analytes that are not amenable to GC or when existing LC methods do not offer sufficient separation power. Many impressive CE separations, including the separation of triazines and sulfonylureas, have been demonstrated in the last few years. The main disadvantages of these techniques are its inadequate detection limits and lack of selective detectors for the determination of residues in environmental matrices. As a result of coupling with SPE, use of CE has become competitive in trace analysis, and the door has been opened to environmental applications in real matrices. Thus, the potential of CE is very good indeed.

See also: **II/Extraction:** Solid-Phase Extraction. **III/Immunoaffinity Extraction. Porous Graphitic Carbon: Liquid Chromatography. Solid-Phase Extraction with Cartridges. Sorbent Selection for Solid-Phase Extraction.**

Further Reading

Barceló D (ed) (1993) *Environmental Analysis. Techniques, Applications and Quality Assurance*. Amsterdam: Elsevier.

Barceló D and Hennion MC (eds) (1997) *Trace Determination of Pesticides and Their Degradation Products in Water*. Amsterdam: Elsevier.

Berrueta LA, Gallo B and Vicente F (1995) A review of solid-phase extraction: basic principles and new developments. *Chromatographia* 40: 474–483.

Csarhárti T and Forgács E (1998) Phenoxyacetic acids: separation and quantitative determination. *Journal of Chromatography A* 717: 157–178.

Dean JR, Wade G and Barnabas IJ (1996) Determination of triazine herbicides in environmental samples. *Journal of Chromatography A* 733: 295–335.

Font G, Mañes J, Moltó JC and Picó Y (1993) Solid phase extraction in multi-residue pesticide analysis of water. *Journal of Chromatography A* 642: 135–161.

International Union of Pure and Applied Chemistry (1994) Analyte isolation by solid-phase extraction (SPE) on silica-bonded phases. Classification and recommended practices. *Pure and Applied Chemistry* 62: 277–304.

Liska I, Kupcik J and Leclercq PA (1989) The use of solid sorbents for direct accumulation of organic compounds from water matrices. A review of solid-phase extraction techniques. *Journal of High Resolution Chromatography* 12: 577–590.

Nollet LML (ed.) (1996) *Handbook of Food Analysis*. New York: Marcel Dekker.

Pichon V (1998) Multiresidues solid-phase extraction for trace analysis of pesticides and their metabolites in environmental waters. *Analusis* 26: M91–M98.

Picó Y, Moltó JC, Mañes J and Font G (1994) Solid phase techniques in the extraction of pesticides and related compounds from food and soils. *Journal of Microcolumn Separations* 6: 331–359.

DropBooks